



# Ceria modified FeMnO<sub>x</sub>—Enhanced performance and sulphur resistance for low-temperature SCR of NOx



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## ABSTRACT

Low-temperature NH<sub>3</sub>-SCR is an environmentally important reaction for the abatement of NO<sub>x</sub> from stationary sources. In recent years FeMnO<sub>x</sub> has attracted significant attention as a potential catalyst for this process, however its catalytic activity and SO<sub>2</sub> resistance require further improvement. In this contribution FeMnO<sub>x</sub> has been modified to examine the effect of ceria on catalytic activity and SO<sub>2</sub> resistance in the low temperature region. Preparation of catalysts via the citric acid method generate modified materials that exhibit enhanced NO turnover compared to FeMnO<sub>x</sub>. A reduction in NH<sub>3</sub> adsorption (NH<sub>3</sub>-TPD) and a suitable ratio between NO sites (NO-TPD) and chemisorbed surface oxygen (XPS) are beneficial for the promotion of fast-SCR. A comparative SO<sub>2</sub> resistance study of FeMnO<sub>x</sub> and Ce(12.5) showed that the latter exhibited improved stability in the presence of SO<sub>2</sub>, as indicated by the retention of pore volume (N<sub>2</sub> adsorption) and surface composition (XPS). *In-situ* DRIFTS demonstrated that chemisorbed N-containing species on Ce(12.5) were much more stable in the presence of SO<sub>2</sub> compared to FeMnO<sub>x</sub>, which resulted in the formation of significantly less metal sulphates and NH<sub>4</sub>HSO<sub>4</sub>.

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## 1. Introduction

Nitrogen oxides NOx (mainly in the form NO and NO<sub>2</sub>) emitted from both stationary (fossil-fueled power plants or FCC units) and mobile sources (gasoline or diesel engines) pose serious environmental problems such as acid rain, photochemical smog, ozone depletion, the greenhouse effect etc. Selective catalytic reduction (SCR) with ammonia is considered the most useful commercialised approach for NOx removal from stationary sources in view of economic and technological efficiency. In recent years, low-temperature SCR catalysts capable of working under conditions at the back-end of the exhaust system have attracted much interest due to their excellent performance and durability [1–8]. However, small concentrations of SO<sub>2</sub> still remain in the flue gas after the electrostatic precipitator (ESP) and desulphurisation devices. SO<sub>2</sub> can further react with NH<sub>3</sub> and O<sub>2</sub> to generate sulphates, which deposit on the surface of the catalyst and cause pore plugging. Of more

serious concern is the chemisorption of SO<sub>x</sub> on the transition metal deNOx catalyst, which are unable to desorb at low temperature resulting in the eventual deactivation of the catalyst via sulphation [9–14]. Preventing or reducing these modes of catalyst deactivation in the low temperature regime is of great interest both industrially and academically for SCR catalysts. Tang et al. found that Fe and V doping into AC/C supported MnO<sub>x</sub>-based monolithic catalysts could improve both low-temperature SCR activity and SO<sub>2</sub> resistance [15]. Kang et al. reported that manganese oxides containing small amounts of copper oxide with a high surface area is the most active catalyst for low temperature NO reduction with NH<sub>3</sub> in the presence of SO<sub>2</sub> [16]. The promotional effect of copper oxide was found to coincide with the formation of the Cu-Mn spinel CuMn<sub>2</sub>O<sub>4</sub>, NO could be oxidised into NO<sub>2</sub> easily via electronic transfer between copper and manganese. Wu et al. found resistance to SO<sub>2</sub> could be significantly enhanced over the Mn/TiO<sub>2</sub> via doping with Ce [17], its addition prevented the formation of Ti(SO<sub>4</sub>)<sub>2</sub> and Mn(SO<sub>4</sub>)<sub>2</sub> and significantly inhibited the deposition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub>. Ke et al. demonstrated that sulphation of active sites on the metal oxide (Co<sub>3</sub>O<sub>4</sub>), resulted in enhanced sulphur resistance within the range of their study [18]. But, no unanimous conclu-

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sions on the mechanism of this enhancement effect can be drawn at present. Kobayashi et al. studied the reactivity and sulphur tolerance of  $V_2O_5$  catalysts supported on  $TiO_2$ - $SiO_2$ - $MoO_3$  (TSM) in low-temperature SCR [6]. The observed enhancement of sulphur tolerance is attributed to significantly reduced  $SO_2$  oxidation activity of the  $V_2O_5$ /(TSM) catalyst, which was ascribed to its increased acidity. Notoya et al. reported that  $SO_2$  was not a poison to  $TiO_2$  and  $ZrO_2$  based catalysts for low-temperature SCR [19], their proposed mechanism suggested that  $SO_2$  contributes to the production of active surface oxygen. This active oxygen was thought to interact with surface  $NO_{ad}$  and form  $NO_{2ad}$ , this species could further react with  $NH_4^{+ad}$  generating  $NH_4NO_{2ad}$ , which would preferentially decompose to  $N_2$ ,  $H_2O$ , and a small amount of NO.

A number of previous studies have examined the activity of bimetallic Mn-based mixed oxides [20,21].  $Cr(0.4)$ - $MnO_x$  prepared by the citric acid method resulted in  $NO_x$  conversions in excess of 98.5% at 120 °C with a GHSV of 30,000 h<sup>-1</sup>. This significant activity was attributed to the formation of the  $CrMn_{1.5}O_4$  phase, which was found to decrease the reduction temperature of manganese oxides [20]. A series of  $FeMnO_x$  catalysts prepared by the citric acid method were examined at 100 °C with a GHSV of 30,000 h<sup>-1</sup>, it was found that the most active catalyst was  $Fe(0.4)Mn(0.6)O_x$ , yielding a  $NO_x$  conversion of 98% with 100%  $N_2$  selectivity. XRD patterns revealed that this high activity occurred in conjunction with the formation of a new crystalline phase,  $Fe_3Mn_3O_8$  [21].

As a non-toxic material,  $CeO_2$  is potentially advantageous for a wide variety of catalytic applications. It can promote structure stability and improve catalytic activity, besides which, oxygen can be stored and released via the redox shift between  $Ce^{4+}$  and  $Ce^{3+}$ , thus the oxidation of NO to  $NO_2$  may be promoted and redox properties may be enhanced [22–25].  $CeO_2$  has been widely used in catalytic applications, especially SCR to remove  $NO_x$  [26–28], however, its application as a low level additive has seldom been explored in this capacity. This study examines a series of  $CeO_x$  doped  $FeMnO_x$  materials for their effectiveness in the removal of  $NO_x$ , resistance to  $SO_2$ ,  $H_2O$  and their combination at low temperature. The observed results for activity and sulphur resistance are further rationalised via the use of a number of different characterisation techniques, to examine physiochemical properties of the surface and bulk structures.

## 2. Experimental

### 2.1. Catalyst preparation

Manganese acetate (99.0%), ferric nitrate (98.5%), ceria (where applicable) and 2 mol L<sup>-1</sup> citric acid (99.5%), where the citric acid to metal ion is 1, were mixed under vigorous stirring at room temperature for 1 h and dried at 120 °C for 12 h. The molar ratio of Mn: Fe was set at 3:2 in this contribution as it was found to be the optimal value previously [21]. The resulting porous, foam-like solid was calcined at 500 °C for 3 h under air in a muffle furnace, after which the resulting catalysts were pressed and sieved to 60–100 mesh and denoted as  $Ce(y)$ , where y is the molar percentage value of  $CeO_x$ .

### 2.2. $NO_x$ SCR activity and $SO_2$ resistance

$NO_x$  SCR activity measurements were carried out in a fixed-bed quartz tube reactor (13 mm i.d. and 430 mm length) with an internal thermocouple to monitor catalyst bed temperature, approximately 2.6 g of catalyst (60–100 mesh) was used for each experiment. The simulated flue gas consisted of, 0.1% NO, 0.1%  $NH_3$ , 3%  $O_2$ , (0.01%  $SO_2$ , 5% or 10%  $H_2O$  when used) and a balance of  $N_2$ , 860 mL min<sup>-1</sup> total flow rate (under ambient conditions) was employed to generate a GHSV of approximately 30,000 h<sup>-1</sup>. Com-

position of the feed gas and effluent stream were continuously monitored using online sensors with emission monitors (SWG-300, MRU, Germany) for analysis of NO,  $NO_2$ , and  $O_2$ . The effluent stream was also analysed via online gas chromatography (4890D, HP, USA), utilising a Porapak Q column to examine the formation of  $N_2O$  and a 0.5 nm molecular sieve column for  $N_2$ . To avoid errors caused by oxidation of ammonia in the converter of the  $NO_x$  analyser, an ammonia trap-containing a phosphoric acid solution was installed before the sample inlet to the flue gas analyser. For  $SO_2$ ,  $H_2O$  and combined  $SO_2$ / $H_2O$  resistance experiments the SCR reaction was allowed to stabilise for 2 h at 120 °C, generating steady-state conditions prior to introducing  $SO_2$ ,  $H_2O$  or their combination into the flue gas. Steady-state  $NO_x$  conversion (1), specific activity (2) and activity (3) were calculated according to the following equations;

$$C(NO_x) = \frac{\varphi(NO_x)_{in} - \varphi(NO_x)_{out}}{\varphi(NO_x)_{in}} \times 100\% \quad (1)$$

$$\text{Specific activity} = \frac{\left(\frac{(\varphi(NO_x)_{in} \times T_f)}{(60 \times 24,000)}\right) \times \left(\frac{(\varphi(NO_x)_{in} - \varphi(NO_x)_{out})}{\varphi(NO_x)_{in}}\right)}{(S_A \times 2.6)} \quad (2)$$

$$\text{Activity} = \left(\frac{(\varphi(NO_x)_{in} \times T_f)}{(60 \times 24,000)}\right) \times \left(\frac{(\varphi(NO_x)_{in} - \varphi(NO_x)_{out})}{\varphi(NO_x)_{in}}\right) \times N_A \quad (3)$$

$\varphi(NO_x) = \varphi(NO) + \varphi(NO_2)$ , and the subscripts *in* and *out* indicate the inlet concentration and outlet concentration at steady state respectively. Specific activity expressed in nmol s<sup>-1</sup> m<sup>-2</sup>, where  $T_f$  is the total flow rate in mL min<sup>-1</sup>, 60 is the number of seconds in a minute, 24,000 mL is the volume occupied by a mole of gas at 25 °C and atmospheric pressure and  $S_A$  is the specific surface area in m<sup>2</sup> g<sup>-1</sup>. Activity is defined by the units s<sup>-1</sup>,  $N_A$  is Avogadro's constant.

Sulphur contaminated catalysts were collected after 4 h SCR reaction in the presence of 100 ppm  $SO_2$ . The  $SO_2$ -containing flue gas was stopped and nitrogen was flowed over the spent catalyst to remove physisorbed species while cooling the reaction to room temperature, at this point the catalyst was removed and stored for further analysis. They are denoted as  $FeMnO_x$ -S and  $Ce(12.5)$ -S, where S indicates the use of  $SO_2$  for 4 h, unless otherwise stated. Multiple experiments have been conducted on all catalysts to determine the error associated with the catalytic data, it has been found that the data varies by a maximum of 2% across 5 variable temperature experiments for each catalyst.

### 2.3. Catalyst characterisation

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX-3A Auto X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Intensity data were collected over a 2 $\theta$  range of 5–85° with a 0.05° step size and an accumulation time of 1 s per step. The XRD phases were identified in comparison with referenced data from the International Centre for Diffraction Data (ICDD) files.

A Micromeritics ASAP 2010 micropore-size analyser was used to measure  $N_2$  adsorption isotherms of the samples at liquid  $N_2$  temperature (−196 °C). The specific surface area was determined from the linear portion of the BET plot, pore-size distribution was calculated from the desorption branch of the  $N_2$  adsorption isotherm using the BJH formula. Prior to surface area and pore-size distribution measurements, all samples were degassed in vacuum at 300 °C for 6 h.

The morphology of the catalysts were measured on a JSM-7401F high resolution field emission scanning electron microscope, at a resolution of 1.5 nm, an accelerating voltage of 0.1–30 kV, an electric current of  $10^{-13}$ – $10^{-9}$  A and a magnification of 25– $10^6$  times.

Spectra were collected with a Horiba Jobin Yvon Lab Tam HR Raman spectrometer equipped with an Olympus BX-41 micro-

scope (objective  $\times 100$ ) and a TE-cooled CCD detector (Andor) in a backscattering configuration utilising a He-Ne laser (632.8 nm excitation line) at a power of 5–20 mV with a spectral resolution of  $0.8\text{ cm}^{-1}$ .

Temperature-programmed reduction (TPR) was performed on a Micromeritics Auto Chem 2920 chemisorption analyser.  $30\text{ mL min}^{-1}$  (NTP) of 10%  $\text{H}_2$  in Ar passed over about 100 mg of sample in a quartz reactor. The heating rate was set at  $8\text{ }^{\circ}\text{C min}^{-1}$  from 25 to  $950\text{ }^{\circ}\text{C}$  for all samples.

$\text{NH}_3$ -,  $\text{NO}$ - and  $\text{SO}_2$ -temperature-programmed desorption (TPD) experiments were performed to determine adsorption/desorption characteristics of each species over the catalyst. 50 mg of each catalyst was loaded in the reactor and was pre-treated in He ( $30\text{ mL min}^{-1}$ ) at  $200\text{ }^{\circ}\text{C}$  for 30 min, then cooled to room temperature in the same stream. The pre-treated sample was then exposed to  $\text{NH}_3$  (2.45%),  $\text{NO}$  (2.47%) or  $\text{SO}_2$  (0.01%) at a flow rate of  $20\text{ mL min}^{-1}$  for 30 min. Physisorbed  $\text{NH}_3/\text{NO}/\text{SO}_2$  was removed by flushing the catalysts with He at a flow rate of  $30\text{ mL min}^{-1}$  for 30 min at  $120\text{ }^{\circ}\text{C}$  prior to TPD. Samples underwent TPD in He ( $30\text{ mL min}^{-1}$ ) from 100 to  $950\text{ }^{\circ}\text{C}$  at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .

X-ray photoelectron spectroscopy (XPS) was performed using a Quantum-2000 Scanning ESCA Microprobe (Physical Electronics) with a hemispherical detector operating at constant pass energy ( $PE = 46.95\text{ eV}$ ). An X-ray source at 210 W ( $I = 15\text{ mA}$ ,  $U = 14\text{ kV}$ ) and Al K $\alpha$  radiation (1486.6 eV) were used. Sample powders were pelletized with a diameter of 0.2 mm and tested at  $20\text{ }^{\circ}\text{C}$ , intensity was determined from the integration of each peak after smoothing and subtraction of the L-shaped background. Binding energies were calculated with reference to the C 1 s peak of contaminant carbon at 284.6 eV with a precision of 0.3 eV. Characteristic peaks were separated utilising peak fitting which was performed using a combination of Gaussian-Lorentzian curves with linear background subtraction. S, C and N counts have not been quantified in this study, total surface concentration is corrected to reflect Ce, Mn, Fe and O only.

*In-situ* diffuse reflectance infrared Fourier transform spectroscopy (*in-situ* DRIFTS) was performed on a FTIR spectrometer (Bruker Vertex 70) equipped with a smart collector and a MCT/A detector cooled by liquid  $\text{N}_2$ . The reaction temperature was controlled precisely via a Pike programmable temperature controller. Prior to each experiment, the sample was pre-treated at  $400\text{ }^{\circ}\text{C}$  for 2 h in  $150\text{ mL min}^{-1}$   $\text{N}_2$  and cooled to  $120\text{ }^{\circ}\text{C}$ . The background spectrum was collected in flowing  $\text{N}_2$  and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows,  $150\text{ mL min}^{-1}$  total flow rate; 0.1%  $\text{NH}_3$ , 0.1%  $\text{NO}$ , 3%  $\text{O}_2$ , (100 ppm  $\text{SO}_2$  when used) with a  $\text{N}_2$  balance. All spectra were recorded by accumulating 64 scans with a resolution of  $4\text{ cm}^{-1}$ .

### 3. Results and discussion

#### 3.1. Low temperature SCR activity of $\text{Ce}(y)$ catalysts

The performances of  $\text{FeMnO}_x$  and  $\text{Ce}(y)$  catalysts prepared by the citrate method were examined in the SCR of  $\text{NO}_x$  with  $\text{NH}_3$  in the presence of excess  $\text{O}_2$  (Fig. 1).  $\text{FeMnO}_x$  exhibited well defined conversion at relatively high GHSV ( $30,000\text{ h}^{-1}$ ). Considering the results obtained at  $75\text{ }^{\circ}\text{C}$  (Fig. 1) it is apparent that the conversion effectively went through a maximum as a function of  $\text{CeO}_x$  level. In this instance 12.5% resulted in the highest conversion of 72%, however, it must be noted that 5–10% doping levels resulted in similar conversion (approximately 63%). At 15%  $\text{CeO}_x$  the conversion was found to decrease below that observed for the base catalyst ( $\text{FeMnO}_x$ ) to 50%. Increasing the temperature resulted in significant improvement in the performance of the catalysts, at  $90\text{ }^{\circ}\text{C}$  the 12.5%  $\text{CeO}_x$  catalyst exhibited a conversion of 97%, whereas the

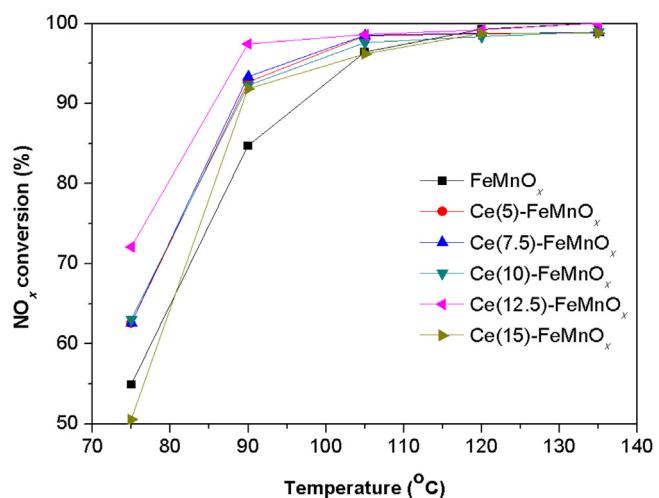


Fig. 1. Low temperature  $\text{NO}_x$  conversion of  $\text{FeMnO}_x$  and  $\text{Ce}(y)$  catalysts ( $y = 5\text{--}15\%$   $\text{CeO}_x$ ), conditions;  $\varphi(\text{NO}) = \varphi(\text{NH}_3) = 0.1\%$ ,  $\varphi(\text{O}_2) = 3\%$ ,  $\text{N}_2$  balance, GHSV =  $30,000\text{ h}^{-1}$ ; reaction temperature =  $75\text{--}135\text{ }^{\circ}\text{C}$ .

other loading levels resulted in approximately 92% indicating that at higher temperatures  $\text{CeO}_x$  addition offers significant promotion over  $\text{FeMnO}_x$  (84%).

#### 3.2. Influence of $\text{SO}_2$ , $\text{H}_2\text{O}$ and their combination

Operations downstream of the desulphurisation unit leads to inherently low levels of  $\text{SO}_2$  in the flue gas however this residual amount would have a negative impact upon the de $\text{NO}_x$  activity of the catalysts. Two different methods can be employed to examine the influence of  $\text{SO}_2$  upon the activity of these catalysts, isothermal and non-isothermal. The latter of which is not particularly suitable for such a study due to the time scales often involved in achieving a stable catalytic state during low-temperature SCR, hence the former at  $120\text{ }^{\circ}\text{C}$  has been employed in this study. After achieving a steady state, 100 ppm  $\text{SO}_2$  was added to the simulated flue gas, all of the catalysts exhibited a decrease in  $\text{NO}_x$  conversion (Fig. 2). The conversion was not found to drop below 90% for any of the catalysts during this study, suggesting that all materials, under the present conditions, exhibit reasonable short term sulphur resistance. However, it showed clearly that all explored catalysts achieve near 100% conversion prior to  $\text{SO}_2$  treatment, making a true comparison in terms of activity impossible as all ceria containing catalysts have similar levels of recovery. But  $\text{FeMnO}_x$  does not significantly recover, indicating a degree of irreversible deactivation occurs over

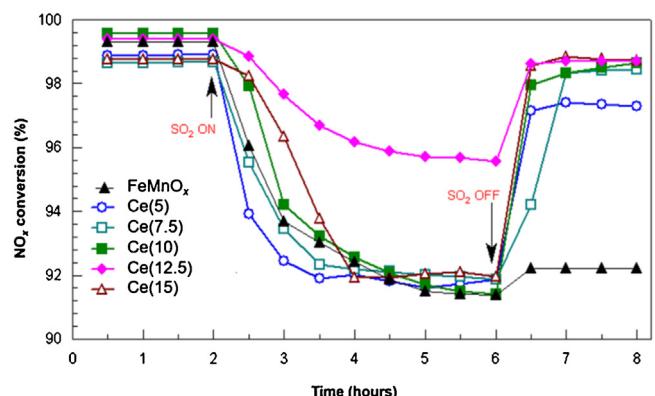
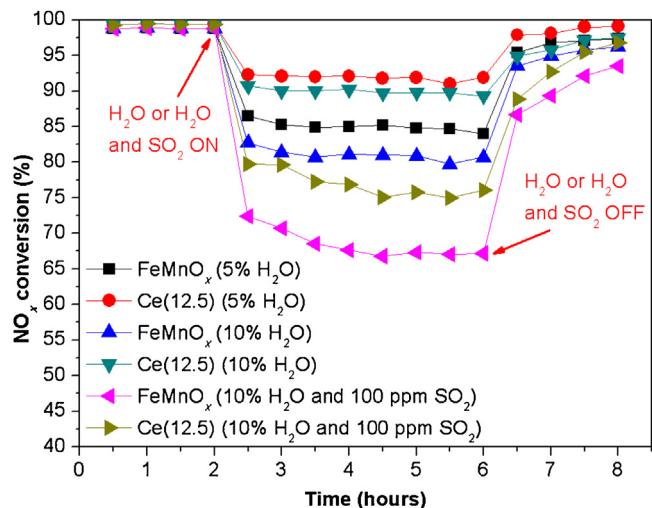


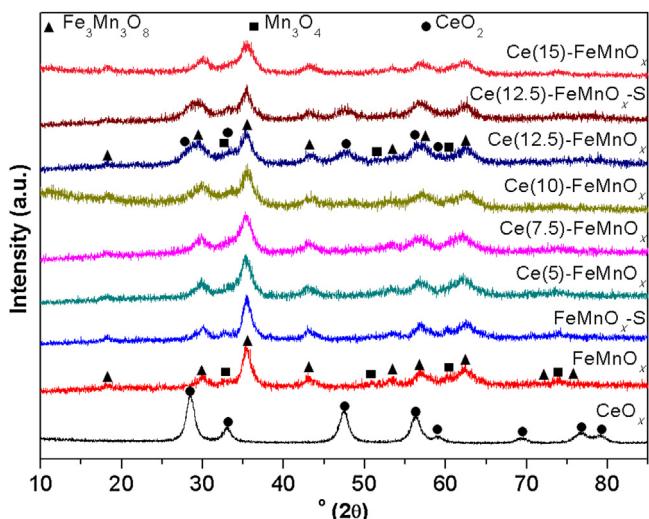
Fig. 2. Influence of  $\text{SO}_2$  on  $\text{NO}_x$  conversion of  $\text{FeMnO}_x$  and  $\text{Ce}(y)$  catalysts ( $y = 5\text{--}15\%$   $\text{CeO}_x$ ), conditions;  $\varphi(\text{NO}) = \varphi(\text{NH}_3) = 0.1\%$ ,  $\varphi(\text{SO}_2) = 100\text{ ppm}$ ,  $\varphi(\text{O}_2) = 3\%$ ,  $\text{N}_2$  balance, GHSV =  $30,000\text{ h}^{-1}$ ; reaction temperature =  $120\text{ }^{\circ}\text{C}$ .



**Fig. 3.** Influence of H<sub>2</sub>O and combined H<sub>2</sub>O and SO<sub>2</sub> on NO<sub>x</sub> conversion of FeMnO<sub>x</sub> and Ce(12.5), conditions;  $\varphi(\text{NO})=\varphi(\text{NH}_3)=0.1\%$ ,  $\varphi(\text{H}_2\text{O})=5\%$  or  $10\%$ ,  $\varphi(\text{SO}_2)=100\text{ ppm}$ ,  $\varphi(\text{O}_2)=3\%$ , N<sub>2</sub> balance, GHSV = 30,000 h<sup>-1</sup>; reaction temperature = 120 °C.

this material. On this basis, the influence of H<sub>2</sub>O and combined H<sub>2</sub>O/SO<sub>2</sub> were explored with FeMnO<sub>x</sub> and Ce(12.5), both of which exhibited obvious difference in their conversions in the presence of SO<sub>2</sub> and their abilities to recover after SO<sub>2</sub> removal.

Examination of the H<sub>2</sub>O and combined H<sub>2</sub>O/SO<sub>2</sub> stability of Ce(12.5) and FeMnO<sub>x</sub> were undertaken (Fig. 3). It can be observed that the FeMnO<sub>x</sub> catalyst exhibits significantly reduced conversion (85%) upon addition of 5% H<sub>2</sub>O to the gas stream, whereas comparatively, the addition of ceria (Ce(12.5)) leads to improved conversion in the presence of H<sub>2</sub>O (93%). Both catalysts possess significant recovery characteristics after stopping H<sub>2</sub>O, indicating that H<sub>2</sub>O does not result in permanent deactivation of either catalyst. Increasing the H<sub>2</sub>O concentration to 10% results in a further decline in NO<sub>x</sub> conversion for both catalysts, however Ce(12.5) still exhibits superior resilience to the effects of H<sub>2</sub>O as indicated by the higher retained conversion (91% vs 81%). In the presence of SO<sub>2</sub> and H<sub>2</sub>O, FeMnO<sub>x</sub> and Ce(12.5) exhibit much lower conversions than those found for just H<sub>2</sub>O or SO<sub>2</sub>, both catalysts exhibit a near complete recovery upon stopping the contaminants. This is particularly impressive for FeMnO<sub>x</sub> as it exhibits minor recovery in the presence of SO<sub>2</sub> alone, suggesting that water helps to reduce irreversible deactivation caused by SO<sub>2</sub>. Zhang et al. examined a TiO<sub>2</sub> supported FeMnO<sub>x</sub> catalyst at significantly higher temperature (320 °C). It was found to possess superior H<sub>2</sub>O resistance compared to the bulk catalyst utilised in this contribution, but it showed negligible recovery in the presence of SO<sub>2</sub> and the combination of SO<sub>2</sub> and H<sub>2</sub>O. The



**Fig. 4.** XRD patterns of as-synthesised CeO<sub>x</sub>, FeMnO<sub>x</sub>, FeMnO<sub>x</sub>-S, Ce(y) catalysts ( $y=5\text{--}15\%$  CeO<sub>x</sub>) and Ce(12.5)-S.

authors ascribe this deactivation effect to the formation of metal sulphates [29], which seems quite probable, as it is known that  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  start decomposing at 270 °C [30]. However, several differences between the two studies are apparent, the  $\text{Fe}_3\text{Mn}_3\text{O}_8$  phase was not observed on the supported catalysts and the temperature employed in the two studies is vastly different. At present the improved recovery in the presence of H<sub>2</sub>O and SO<sub>2</sub> cannot be readily explained, further work is currently ongoing with this and a related system in an attempt to rationalise this effect.

### 3.3. XRD analysis

XRD was used to examine the crystalline phases present in the catalysts (Fig. 4), comparative crystallite sizes were calculated using the Scherrer equation on the reflection  $ca. 35.0^{\circ} 2\theta$  for  $\text{Fe}_3\text{Mn}_3\text{O}_8$  and  $28.5^{\circ} 2\theta$  for  $\text{CeO}_2$  (Table 1). It was apparent that the CeO<sub>x</sub> sample exhibited diffraction peaks (Fig. 4) coinciding with the face centred cubic (fcc) fluorite structure  $\text{CeO}_2$  (ICDD PDF card # 65-2975). Its major characteristic diffraction peaks occur at  $28.5^{\circ}$ ,  $33.1^{\circ}$ ,  $47.5^{\circ}$  and  $56.3^{\circ} 2\theta$ , which correspond with reflections of the (111), (200), (220) and (311) crystallographic planes respectively. Examination of the FeMnO<sub>x</sub> sample indicates the presence of mixed phases, the major contributing crystalline phase could be attributed to the formation of the  $\text{Fe}_3\text{Mn}_3\text{O}_8$  phase (ICDD PDF card # 75-0034 =  $35.0^{\circ}$ ,  $56.2^{\circ}$  and  $61.7^{\circ} 2\theta$ ) and  $\text{Mn}_3\text{O}_4$  (ICDD PDF card # 89-4837  $2\theta = 32.3^{\circ}$ ,  $36.1^{\circ}$  and  $59.9^{\circ} 2\theta$ ). Determination of the  $\text{Mn}_3\text{O}_4$  phase proved to be quite difficult due to the combi-

**Table 1**  
Surface area, pore volume, pore diameter, crystallite size and specific activity of as-synthesised CeO<sub>x</sub>, FeMnO<sub>x</sub>, FeMnO<sub>x</sub>-S, Ce(y) catalysts ( $y=5\text{--}15\%$  CeO<sub>x</sub>), Ce(12.5)-S (4 h) and (12 h).

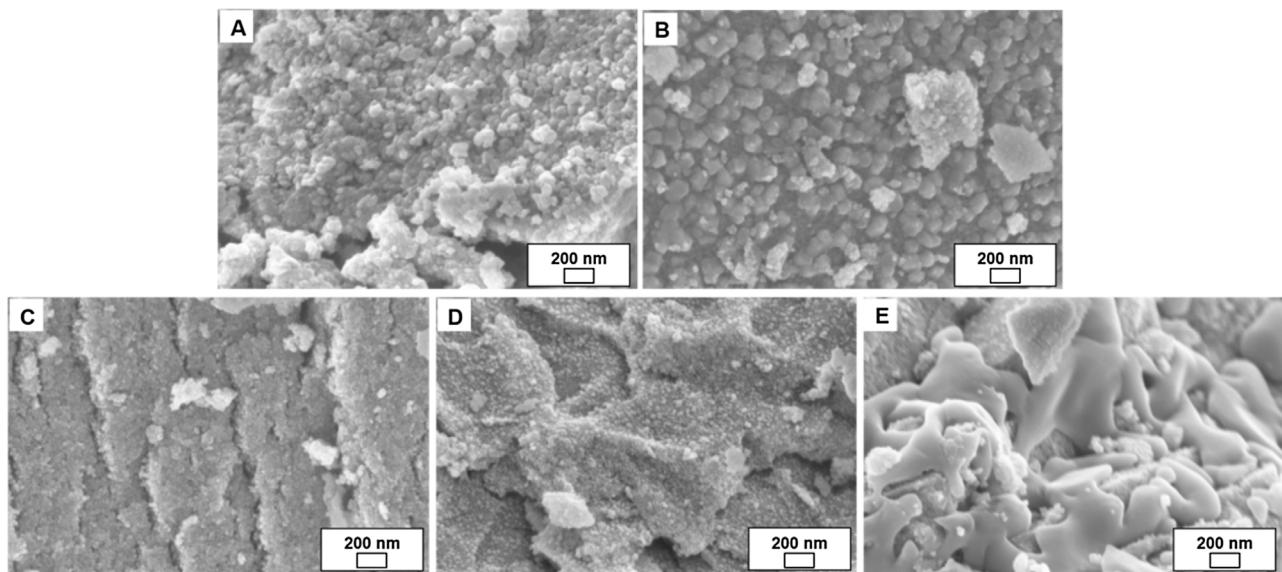
	BET surface area( $\text{m}^2\text{g}^{-1}$ )	Pore volume ( $\text{cm}^3\text{g}^{-1}$ )	Average pore diameter(nm)	Crystallite size (nm) <sup>b</sup>	Specific activity ( $\text{nmols}^{-1}\text{m}^{-2}$ ) <sup>c</sup>
CeO <sub>x</sub>	62	0.040	4.71	39	–
FeMnO <sub>x</sub>	55 <sup>d</sup> (35)	0.090 <sup>d</sup> (0.067)	5.88 <sup>d</sup> (6.37)	33	2.3
Ce(5.0)	68	0.076	5.00	28	2.1
Ce(7.5)	70	0.087	4.98	26	2.1
Ce(10.0)	66	0.072	5.48	26	2.2
Ce(12.5)	59 <sup>d</sup> (52) <sup>a</sup> (34)	0.082 <sup>d</sup> (0.082) <sup>a</sup> (0.073)	5.83 <sup>d</sup> (5.84) <sup>a</sup> (5.85)	25 <sup>d</sup> (23)	2.8
Ce(15.0)	73	0.115	5.47	22	1.8

<sup>a</sup> Obtained after 12 h of deNO<sub>x</sub> in the presence of 100 ppm SO<sub>2</sub>.

<sup>b</sup> Calculated from Fig. 3 via the Scherrer equation.

<sup>c</sup> Specific activity calculated per unit area ( $\text{m}^2$ ), correcting for the use of 2.6 g of catalyst.

<sup>d</sup> Data listed in the parentheses were obtained after 4 h of deNO<sub>x</sub> in the presence of 100 ppm SO<sub>2</sub>.



**Fig. 5.** SEM images of as-synthesised  $\text{FeMnO}_x$  (A),  $\text{FeMnO}_x\text{-S}$  (B), as-synthesised  $\text{Ce}(12.5)$  (C),  $\text{Ce}(12.5)\text{-S}$  (4 h) (D) and  $\text{Ce}(12.5)\text{-S}$  (12 h) (E).

nation of broad, low intensity diffraction peaks, however, a peak was found to exist in a relatively isolated region of the diffraction pattern (approximately  $74.5^\circ 2\theta$ ).

Examination of 5 and 7.5%  $\text{CeO}_x$  modified catalysts indicates phases related to crystalline  $\text{CeO}_2$  were not observed, suggesting that it was present in an amorphous, highly dispersed phase. The isolated peak corresponding to  $\text{Mn}_3\text{O}_4$  was still present at these loading levels appearing to have broadened, indicating a smaller crystallite size. An increase in  $\text{CeO}_x$  content (10%) resulted in a material which exhibited crystalline  $\text{CeO}_2$ , as evidenced by the appearance of a low intensity diffraction peak at  $47.5^\circ 2\theta$ . The XRD pattern of  $\text{Ce}(12.5)$  demonstrated that larger ceria crystallites were present on the catalyst, in addition to the apparent loss of the crystalline  $\text{Mn}_3\text{O}_4$  phase. The major  $\text{CeO}_2$  diffraction peak had shifted to higher diffraction angle compared to the standard ceria sample ( $47.5^\circ 2\theta$ ) suggesting incorporation of a smaller metal ion into the ceria lattice [31,32]. It was found that  $\text{Ce}(15)$  exhibited no ceria diffraction peaks, in conjunction with the reappearance of the crystalline  $\text{Mn}_3\text{O}_4$  phase. Increased amounts of  $\text{CeO}_x$ , resulted in a general reduction of the  $\text{Fe}_3\text{Mn}_3\text{O}_8$  crystallite size, which is similar to the results obtained by Huang et al. for  $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2$  [28]. Based upon previous observations of the active phase in  $\text{FeMnO}_x$ , it is suggested that the enhancement in conversion may arise due to the formation of a secondary or new active phase which is attributed to a  $\text{CeO}_x$  solid solution. Examination of both  $\text{FeMnO}_x$  and  $\text{Ce}(12.5)$  after deNO<sub>x</sub> in the presence of SO<sub>2</sub>, indicates no obvious change in their diffraction patterns, suggesting that no crystalline sulphate phases were formed.

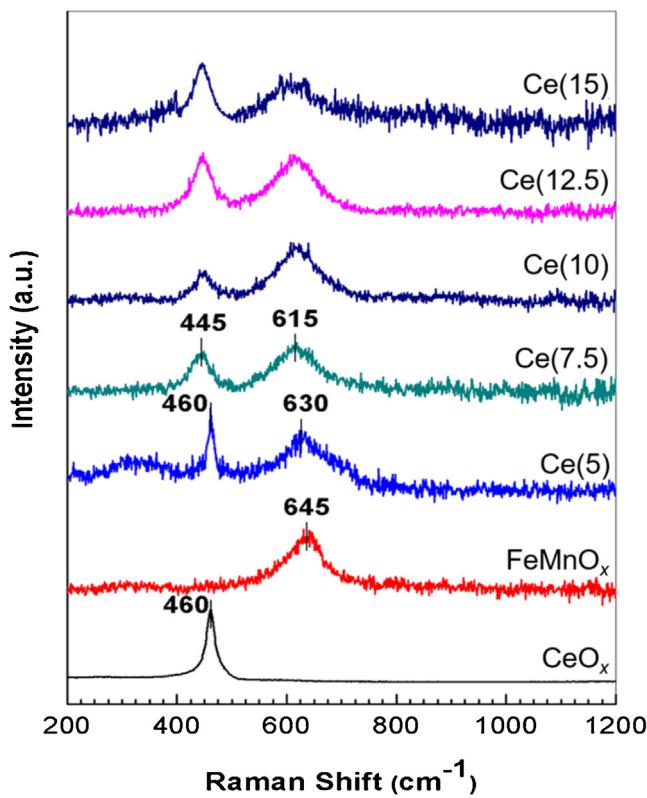
#### 3.4. BET, BJH and SEM analysis

$\text{N}_2$  adsorption was utilised to determine the surface area, pore-based characteristics and specific activity in relation to surface area of the catalysts. All catalysts containing ceria exhibited higher surface area than the standard bimetallic oxide catalyst (Table 1), however, no obvious trend was found relating increased amounts of  $\text{CeO}_x$  incorporation to surface area, pore volume or average pore diameter. It was found that the most active catalyst at  $75^\circ\text{C}$  ( $\text{Ce}(12.5)$ ) possessed the second lowest surface area and crystallite size, while  $\text{Ce}(15)$  had the highest surface area, smallest crystallite size and specific activity. These results indicate that enhanced

low temperature activity is not attributable to the generation of an increased number of active sites via surface area enhancement and that a complex interplay exists between properties such as, crystal phases, amorphous phases, localised surface structure and composition.

After 4 h treatment with 100 ppm SO<sub>2</sub>, catalysts were characterised to examine any alterations to the textural properties due to the deactivation phenomena observed in Fig. 2. It was found that both  $\text{FeMnO}_x$  and  $\text{Ce}(12.5)$  exhibit surface area losses during SO<sub>2</sub> treatment (Table 1). It has been demonstrated that  $\text{FeMnO}_x$  exhibits an unrecoverable loss in conversion and also a significant reduction in surface area ( $55\text{--}35 \text{ m}^2 \text{ g}^{-1}$ ), which is associated with pore blockage, as indicated by the decrease in pore volume and increase in the average pore diameter. SEM of  $\text{FeMnO}_x$  prior to and after exposure to SO<sub>2</sub> (Fig. 5A and B respectively), indicates a minor degree of aggregation at the surface, however little can be ascertained regarding the change in pore structure from this technique due to the relatively small size of the pores.  $\text{Ce}(12.5)$  exhibits a lower surface area loss ( $59\text{--}52 \text{ m}^2 \text{ g}^{-1}$ ), in conjunction with no obvious change in the pore structure. (Table 1). On the basis of SEM imaging it can be observed that the as-synthesised catalyst (Fig. 5C) exhibited quite a high degree of surface defects on the bulk particle, after exposure to SO<sub>2</sub> for 4 h (Fig. 5D) there were fewer observed. After 12 h (Fig. 5E) the surface had changed drastically, becoming relatively defect-free, which coincided with a significant decrease in surface area ( $33 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume (Table 1).

Supported vanadia catalysts are highly susceptible to the formation of  $\text{NH}_4\text{HSO}_4$ , which is known to deposit readily on the surface of the catalyst, blocking the pores [30,33]. Recently Kwon et al. compared vanadia supported on  $\text{Ti}_{1-x}\text{Ce}_x\text{O}_{2-s}$  with  $\text{TiO}_2$  in SO<sub>2</sub> contaminated SCR, they demonstrated that the presence of Ce species led to an improvement in SO<sub>2</sub> resistance of the catalyst. It was suggested that the formation of  $\text{Ce}_2(\text{SO}_4)_3$  led to significant consumption of SO<sub>2</sub>, which inhibited the formation of  $\text{NH}_4\text{HSO}_4$ , resulting in a longer lifetime [30]. Mn and Fe-based catalysts are also known to be susceptible to the formation of  $\text{NH}_4\text{HSO}_4$  and stable metal sulphates, which significantly decreases the reducibility of the metal ion species [34].  $\text{FeMnO}_x$  may deactivate via pore plugging due to  $\text{NH}_4\text{HSO}_4$ , however the formation of metal sulphate/sulphite cannot be ruled out. The modified catalyst is found to be more susceptible to surface modification, possibly via the for-

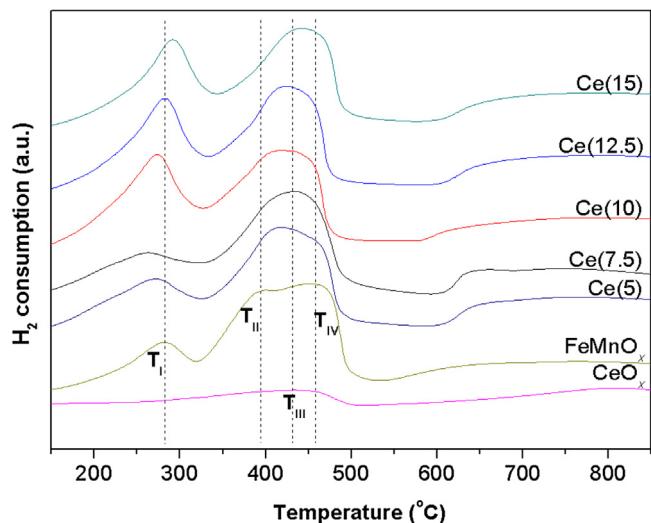


**Fig. 6.** Raman spectra of as-synthesised CeO<sub>x</sub>, FeMnO<sub>x</sub> and Ce(y) catalysts (y = 5–15% CeO<sub>x</sub>).

mation of metal sulphates during exposure to SO<sub>2</sub>, no obvious loss in pore volume was observed over the initial four hour reaction period suggesting that NH<sub>4</sub>HSO<sub>4</sub> formation was suppressed.

### 3.5. Raman analysis

Raman spectroscopy (Fig. 6), is a suitable technique to examine variations in vibrational modes associated with CeO<sub>2</sub> and FeMnO<sub>x</sub> as ceria content increased. Cubic CeO<sub>2</sub> displays an intense band at approximately 460 cm<sup>-1</sup>, which is consistent with previous publications [35,36] and is assigned to the symmetric breathing mode of O atoms around Ce<sup>4+</sup> [37,38]. Fe(0.4)-MnO<sub>x</sub> exhibits a single signal corresponding to Fe<sub>3</sub>Mn<sub>3</sub>O<sub>8</sub> and Mn<sub>3</sub>O<sub>4</sub> at 645 cm<sup>-1</sup>, which is attributed to the vibration of Mn-O [21,39]. No evidence of amorphous Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> was found in the wavenumber range 200–400 cm<sup>-1</sup>, suggesting that Fe species had been fully incorporated into the Fe<sub>3</sub>Mn<sub>3</sub>O<sub>8</sub> structure [40,41]. Addition of ceria (5%), resulted in no obvious shift or broadening in the signal ca. 460 cm<sup>-1</sup>, however, the Mn-O vibrational mode was shifted to 630 cm<sup>-1</sup>. As the amount of ceria increased to 7.5% both bands shifted to lower wavenumbers (445 cm<sup>-1</sup> and 615 cm<sup>-1</sup> respectively), beyond this level no further change in either peak position was observed. Broadening of the band associated with CeO<sub>2</sub> indicates that either metal ions were incorporated into the lattice [39] or ceria crystallites were reduced in size [20]. The appearance of broad diffraction peaks for Ce(10) and Ce(12.5) (Fig. 4) with no narrowing of the Raman band negates the latter argument. The apparent red shift of the signal position is attributed to lattice contraction [32], due to the incorporation of smaller metal ions (Mn and/or Fe) into the ceria lattice. Venkataswamy et al. demonstrated that the formation of Fe/Mn doped ceria resulted in a new band arising at 594–597 cm<sup>-1</sup>, which was attributed to oxygen vacancies within the ceria lattice [39]. They suggested that a band at 644 cm<sup>-1</sup> for Mn-doped ceria

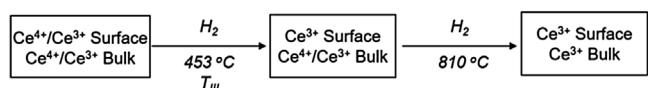


**Fig. 7.** TPR profiles of as-synthesised CeO<sub>x</sub>, FeMnO<sub>x</sub> and Ce(y) catalysts (y = 5–15% CeO<sub>x</sub>).

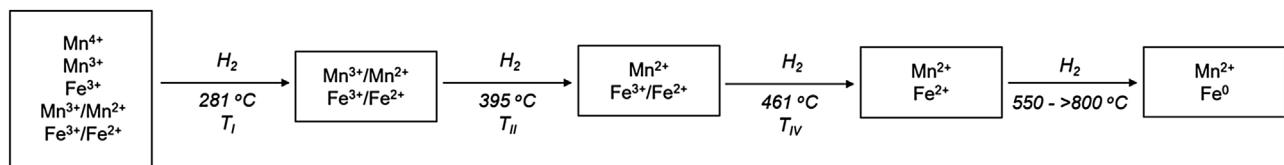
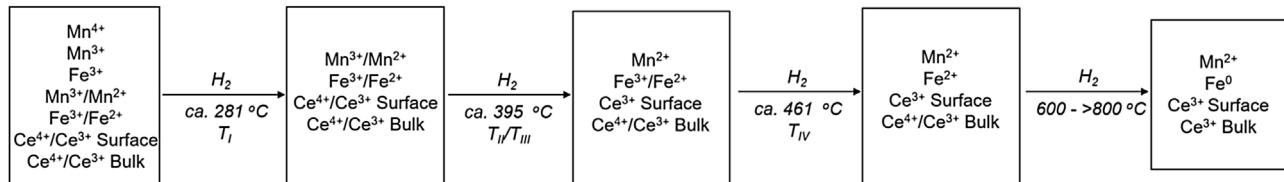
was also associated with oxygen vacancies, however this is most likely associated with amorphous MnO<sub>x</sub> species present on the surface of the catalyst. Given the relatively low concentration of ceria, moderate signal to noise ratio, broad bands and the occurrence of the Mn-O vibration mode, the signal assigned to oxygen vacancies was not observed in this study. The red shift in the band ca. 645 cm<sup>-1</sup> may be associated with reduction of the Fe<sub>3</sub>Mn<sub>3</sub>O<sub>8</sub> crystallite size. Care must be taken making this suggestion due to the influence other factors upon band position, broadness and intensity [20]. Raman spectroscopy verifies the formation of a solid solution, which agrees well with XRD, however, questions still remain regarding its influence upon activity. In an attempt to probe changes in activity and sulphur resistance, bulk properties, such as reducibility (a critical parameter for redox catalysis) must be examined.

### 3.6. TPR analysis

TPR profiles are presented in Fig. 7 for all catalysts and CeO<sub>x</sub>, it can be observed that the latter generates two peaks ca. 453 (denoted as T<sub>III</sub> in Fig. 7) and 810 °C, which can be assigned to the reduction of surface and bulk Ce<sup>4+</sup> respectively (summarised in Scheme 1) [31,32]. Based upon our previous work, MnO<sub>x</sub> exhibits two reduction events, a small feature ca. 187 °C and a much broader asymmetric feature at around 439 °C [42]. A similar TPR profile was observed by Yang et al. who suggested that this represented the reduction of Mn<sub>3</sub>O<sub>4</sub> via two steps. The first step was said to be associated with the reduction of a weaker Mn-O bond, which yielded a more recalcitrant structure, resulting in further reduction at higher temperature [43]. However sufficient evidence was not provided to support the claim of this new intermediate MnO<sub>x</sub> structure. Several authors have provided a different explanation, suggesting that amorphous Mn<sub>2</sub>O<sub>3</sub> initially reduces to Mn<sub>3</sub>O<sub>4</sub> before converting to MnO at higher temperature [42,44], this is the more likely of the two proposals and hence will be considered as the reductive process for MnO<sub>x</sub>. FeO<sub>x</sub> is found to exhibit three major reduction features at 362, 638 and above 700 °C, which are associated with the reduc-



**Scheme 1.** Reduction stages of CeO<sub>x</sub>.

Scheme 2. Reduction stages of  $\text{FeMnO}_x$ .Scheme 3. Reduction stages of  $\text{Ce}(y)$  catalysts ( $y = 5\text{--}15\%$   $\text{CeO}_x$ ).

tion of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$  and  $\text{FeO}$  to  $\text{Fe}^0$  [42].  $\text{FeMnO}_x$  has a more complex TPR profile with three very broad reduction features, the first is observed starting below  $150^\circ\text{C}$  and maximises at approximately  $281^\circ\text{C}$ . The second is a highly asymmetric feature which intersects the initial reduction and is observed between  $325$  and  $525^\circ\text{C}$ , based upon the shape of the peak, it seems that at least two reductive transitions occur in this region (these features are denoted as  $T_1$ ,  $T_{II}$  and  $T_{IV}$  respectively, in Fig. 7). The final feature begins at  $550^\circ\text{C}$  and continues beyond  $800^\circ\text{C}$ . On the basis of XRD data it can be determined that the major crystalline phases may be attributed to  $\text{Fe}_3\text{Mn}_3\text{O}_8$  and  $\text{Mn}_3\text{O}_4$ . Work undertaken by Chen et al. demonstrates that a physical mixture of  $\text{MnO}_x$  and  $\text{FeO}_x$  results in a lowering of the reduction temperature for the  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$  and  $\text{FeO}$  to  $\text{Fe}^0$  transitions, however little change was observed for the  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  reduction. It must be noted that the lower temperature reduction observed for  $\text{MnO}_x$  was shifted to significantly higher temperature in conjunction with a minor temperature decrease in the  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}$  transition [42]. With these previous observations in mind the reductions observed for  $\text{FeMnO}_x$  can be assigned as follows, the initial feature (*ca.*  $281^\circ\text{C}$ ) is attributed to the transformation of high oxidation state ions, namely those associated with  $\text{Mn}^{4+}/\text{Mn}^{3+}$  and perceptibly  $\text{Fe}^{3+}$  in easily reducible sites. The broad feature between  $325$  and  $525^\circ\text{C}$  is associated with numerous different reductive transitions, in the lower temperature region reductions associated with  $\text{Mn}^{3+}$  in  $\text{Fe}_3\text{Mn}_3\text{O}_8$  and  $\text{Mn}_3\text{O}_4$  phases, the higher temperature region of this feature is attributed to the transition of  $\text{Fe}^{3+}$  in  $\text{Fe}_3\text{Mn}_3\text{O}_8$  to  $\text{Fe}^{2+}$ . The final feature is assigned to the reduction of  $\text{Fe}^{2+}$  to  $\text{Fe}^0$  (summarised in Scheme 2).

The addition of ceria results in significant improvement of low temperature reducibility (Fig. 7), the feature ( $T_1$ ) is found to broaden significantly, with maximised hydrogen consumption achieved at lower temperature, which is optimised at 7.5 mol% ceria. Further addition of ceria results in a significant enhancement in the intensity of this feature suggesting that, more, higher oxidation state species are reduced at lower temperature. It is rather obvious that the broad feature observed for  $\text{FeMnO}_x$  changes drastically as ceria content increased, indicating that reducibility of the catalyst improves. Based upon the assigned reductions in this range (Scheme 2) it can be observed that the transitions associated with the spinel-type structures occur in this region. As mentioned previously the lower temperature range ( $T_{II}$ ) is assigned to the reduction of  $\text{Mn}^{3+}$  species in  $\text{Fe}_3\text{Mn}_3\text{O}_8$  and  $\text{Mn}_3\text{O}_4$  and at higher temperature ( $T_{IV}$ ) the Fe species in  $\text{Fe}_3\text{Mn}_3\text{O}_8$ . It is apparent that the shift in the feature is towards higher temperature ( $T_{IV}$ ), suggesting that there is a decline in the lower temperature contribution ( $T_{II}$ ) with ceria addition. On this basis it may be suggested that Mn-species are preferentially incorporated into the ceria lattice in comparison

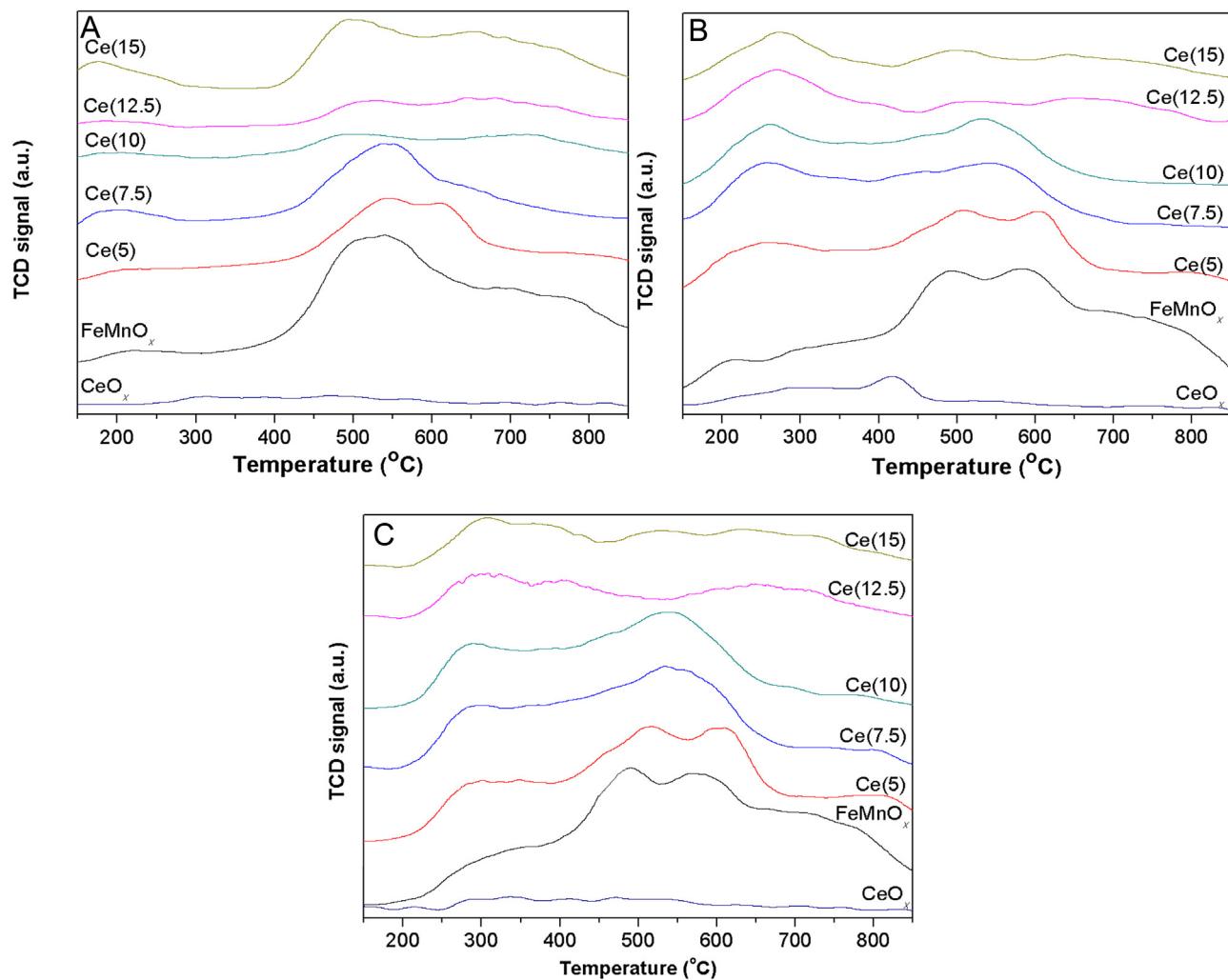
**Table 2**  
 $\text{NH}_3$ -,  $\text{NO}$ - and  $\text{SO}_2$ -TPD peak areas for  $\text{CeO}_x$ ,  $\text{FeMnO}_x$  and  $\text{Ce}(y)$  catalysts ( $y = 5\text{--}15\%$ ).

Catalyst	Total desorption peak area ( $\text{mVs}^{-1}$ )		
	$\text{NH}_3$ -TPD	$\text{NO}$ -TPD	$\text{SO}_2$ -TPD
$\text{CeO}_x$	1006	2696	–
$\text{FeMnO}_x$	22092	23510	18593
$\text{Ce}(5)$	11986	12251	14940
$\text{Ce}(7.5)$	11967	11076	11643
$\text{Ce}(10)$	5417	12345	11375
$\text{Ce}(12.5)$	5158	8102	5660
$\text{Ce}(15)$	10329	7877	6055

to Fe-species. This would certainly match the apparent increase in reducibility ( $T_1$ ) and aligns well with observations made by Ramana et al., who demonstrate that  $\text{Ce}_{1-x}\text{Mn}_x\text{O}_{2-\sigma}$  catalysts exhibit significantly enhanced  $T_1$  reduction peaks and smaller mid-temperature peaks ( $T_{II}$ ) [32]. It was found that the incorporation of Fe into ceria resulted in an enhancement effect in the mid temperature region (comparable to  $T_{II}$ ) [32], however this is not exhibited by the data within this contribution. It must be noted that both Ramana et al. and Venkataswamy et al. found no separate reduction feature attributed to surface  $\text{Ce}^{4+}$ , suggesting that this must occur within the same range as that observed for both the Fe and Mn reductions [32,39]. It can be determined that the reducibility of surface  $\text{Ce}^{4+}$  is enhanced and occurs in the mid-temperature range ( $T_{II}$ ). Bulk  $\text{Ce}^{4+}$  was found to reduce in a similar region to that observed for ceria by Ramana et al., a notable feature is present at temperatures above  $600^\circ\text{C}$  in Fig. 7, which may be associated with both  $\text{Fe}^{2+}$  to  $\text{Fe}^0$  and bulk  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  reductive transitions (summarised in Scheme 3) [32].

### 3.7. $\text{NH}_3$ -, $\text{NO}$ - and $\text{SO}_2$ -TPD

To gain further insight into these complex structure-activity relationships, a series of TPD experiments were conducted to compare desorption characteristics of chemisorbed  $\text{NH}_3$  (Fig. 8A), for the purposes of comparison the total desorption area was tabulated for each catalyst (Table 2). It can be observed in Fig. 8A that  $\text{CeO}_x$  exhibits a very broad low intensity desorption profile. Hence, it is apparent that  $\text{CeO}_x$  exhibits a relatively low number of acid sites possessing a large variance in strength, which is in very good agreement with results obtained by Shen et al. [45].  $\text{FeMnO}_x$  exhibits a profile indicative of a large number of total acid sites, in the weak acid strength region one very small desorption peak can be observed centering around  $210^\circ\text{C}$ , at higher temperatures a very broad desorption trace is observed from approximately  $300\text{--}850^\circ\text{C}$ . The latter appears to exhibit four potential features *ca.* 500, 550, 700



**Fig. 8.** NH<sub>3</sub>- (A), NO— (B) and SO<sub>2</sub>-TPD (C) of as-synthesised CeO<sub>x</sub>, FeMnO<sub>x</sub> and Ce(y) catalysts (y = 5–15% CeO<sub>x</sub>).

and 775 °C, which coincides with the removal of strongly bound ammonia on acid sites, this clearly indicates the presence of a significant spectrum of acid site strengths and, by association, a large number of differing acid site species and/or environments. Upon addition of CeO<sub>x</sub> (5%) a large reduction in overall signal intensity (Table 2) was observed, indicating a significant loss of acidic character. Fig. 8A shows that a general reduction in all acid sites occurs, however a significant decline in the feature at 500 °C and the appearance of a reductive transition at 625 °C. An increase in CeO<sub>x</sub> loading to 7.5% resulted in minor reduction of the peak area (Table 2), however a significant change in Fig. 8A was apparent indicating a noticeable decrease in intensity of the peak at 625 °C and an increase in the lower temperature peaks ca. 210 and 550 °C. Ce(10) and Ce(12.5) result in significantly reduced desorption profiles, suggesting a significant loss in the number of acid sites on the catalyst. Upon increasing the loading to 15% the amount of desorbed NH<sub>3</sub> increased significantly (Table 2). This increase in NH<sub>3</sub> desorption coincides with the re-emergence of crystalline Mn<sub>3</sub>O<sub>4</sub>, which was not observed to any degree at 10 and 12.5% ceria addition. Deorsola et al. found that MnO<sub>x</sub> catalysts which contained crystalline Mn<sub>3</sub>O<sub>4</sub> exhibited significantly enhanced NH<sub>3</sub>-TPD patterns, suggesting that this phase enhances the acidity of the catalysts [46]. These results tentatively suggest that low levels of ammonia adsorption is a key characteristic of catalysts exhibiting higher low-temperature SCR activity, but, this parallels findings made in

TPR studies in that catalysts containing both 10 and 12.5% CeO<sub>x</sub> appear to exhibit this optimised characteristic.

It has been suggested previously that the most important facet of low-temperature SCR is the initial oxidation of NO to NO<sub>2</sub> [20]. This was later challenged by Salazar et al. who suggested, via the utilisation of active component separation, that the initial process generates a more labile species, such as HNO<sub>2</sub> [47]. Regardless of the exact species, it is agreed by both that NO oxidation is an important mechanistic step in the SCR process. An examination of the NO-TPD properties of all catalysts was undertaken (Fig. 8B), it can be observed that CeO<sub>x</sub> exhibits a broad desorption feature from approximately 175–600 °C with several maxima ca. 275 °C (nitrosyl species) and 425 °C (metal nitrate) [48]. However, the overall signal intensity was low in comparison to the other catalysts (Table 2). FeMnO<sub>x</sub> generates a significant desorption profile (Fig. 8B) exhibiting three features (210, 490 and 590 °C), suggesting a number of NO<sub>ads</sub> species are present in different chemical environments. The addition of ceria exhibits a pronounced effect upon this profile, indicating an increase in the contribution from lower temperature desorption. Conversely the two higher temperature features initially reduce in intensity upon addition of 5% CeO<sub>x</sub> and above this loading a single feature which gradually shifts towards lower temperature is formed. Similar observations were made by Lee et al. where it was found that the addition of ceria to Sb-V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> led to significant improvement in low temperature desorption char-

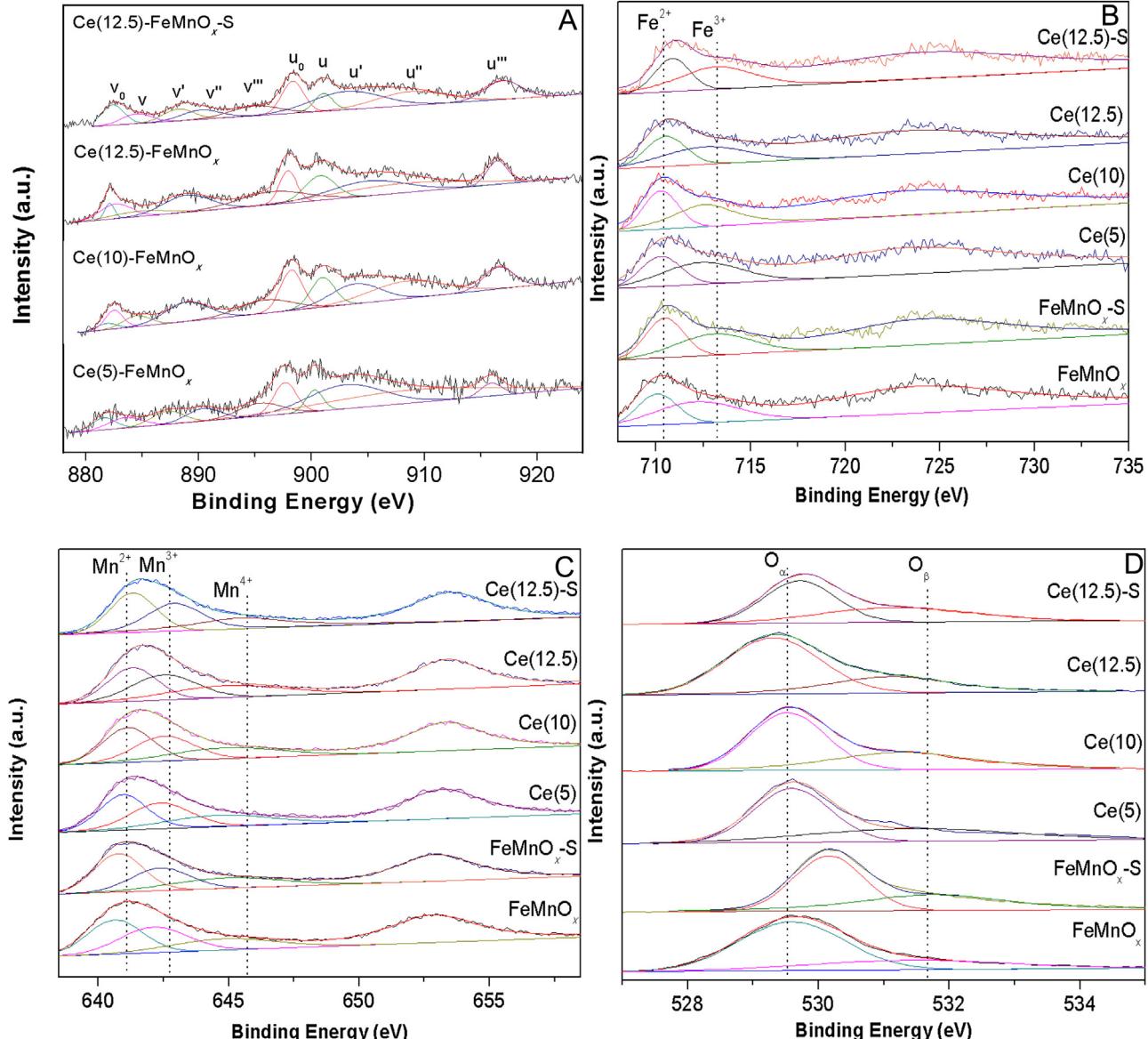
acteristics of their catalysts [49]. However some differences are apparent, the aforementioned study exhibits an increase in total acidity upon addition of ceria, whereas these systems are bulk catalysts with a support based additive. It is suggested that the results in this study occur due to ceria interacting with the particles, effectively blocking large portions of the active surface, while simultaneously improving its activity. Doping of  $Mn^{x+}$  and  $Fe^{x+}$  into ceria and surface modification of accessible  $Fe_3Mn_3O_8$  via geometric and/or electronic interactions commonly observed in Ce/Cu based systems are expected to play a key role in this enhancement effect [31,32,50]. Hence, it can be determined that the desorption features which appear to be beneficial for enhanced low temperature activity are those that exhibit relatively low levels of  $NH_3$  desorption at moderate temperature and which exhibit significant low temperature NO desorption, with minimal moderate and high temperature contributions.

Examination of the  $SO_2$ -TPD profile (Fig. 8C) for ceria reveals only a very small desorption contribution observed across the range, which maximises between 200 and 600 °C. It has been reported that ceria is able to inhibit the formation of  $NH_4HSO_4$

**Table 3**  
Surface atomic concentration of  $FeMnO_x$ ,  $FeMnO_x$ -S,  $Ce(y)$  ( $y = 5, 10$  and  $12.5\%$ ) and  $Ce(12.5)$ -S.

Catalyst	Surface concentration (atm.%)				
	Ce	Fe	Mn	O	$Fe/(Fe + Mn)$
$FeMnO_x$	—	10.83	22.27	66.90	0.33
$FeMnO_x$ -S	—	7.92	22.34	69.74	0.26
$Ce(5)$	0.38	7.51	18.09	74.02	0.29
$Ce(10)$	0.56	7.04	17.01	75.40	0.29
$Ce(12.5)$	0.68	8.23	19.37	71.72	0.30
$Ce(12.5)$ -S	0.48	7.62	18.29	73.61	0.29

during reaction [51]. It has also been demonstrated that ceria containing Mn or Fe catalytic systems efficiently utilise  $SO_2$  to generate additional acidic properties, while effectively protecting metal ions associated with NO adsorption (Fe and/or Mn) [52,53].  $FeMnO_x$  exhibits the most intense TPD profile, with several desorption events observed at 350, 490, 575, 725 and 775 °C. The feature observed at 350 °C, is attributed to the removal of  $SO_2$  species adsorbed on weakly acidic centres as suggested by Kijlstra et al.



**Fig. 9.** XPS analysis of Ce (A), Fe (B), Mn (C) and O (D) for as-synthesised  $FeMnO_x$ ,  $Ce(y)$  ( $y = 5, 10$  and  $12.5\%$ ) and  $Ce(12.5)$ -S.

[54]. It was found by Siriwardane et al. that thermal decomposition of both  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  occurred across the same temperature range (500–600 °C) [55], however they exhibited different profiles.  $\text{FeSO}_4$  generated a more intense mass loss initially, whereas more mass loss was found at higher temperatures for  $\text{Fe}_2(\text{SO}_4)_3$ . Hence it is suggested that the observed TPD features at 490 and 575 °C are associated with decomposition of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sulphate species respectively. Higher temperature features are found to be in the range expected for decomposition of manganese sulphate, Wu et al. demonstrated that  $\text{MnSO}_4$  decomposed between 750 and 900 °C [56]. It is tentatively suggested that due to the different  $\text{Mn}^{2+}$  sites present in the catalyst, namely those associated with  $\text{Fe}_3\text{Mn}_3\text{O}_8$  and  $\text{Mn}_3\text{O}_4$ , that the two features ca. 725 and 775 °C are attributable to the decomposition of sulphate species in different chemical environments. Increased ceria content results in an overall reduction in  $\text{SO}_2$  desorption, which maximises at 12.5% addition (Table 3). Similarly a comparison of TPD profiles demonstrates that ceria promotes lower temperature desorption with a simultaneous reduction in higher temperature contributions, this effect is most apparent for Ce(12.5) and Ce(15).

Hence, these results demonstrate that ceria addition significantly alters the bulk properties of the catalysts, specifically those associated with adsorption/desorption, which are key parameters for catalytic activity. The addition of ceria results in a significant decrease in the number of available adsorption sites, it is apparent that the remaining redox sites become more active suggesting a synergistic interaction exists at 12.5% that is not completely apparent at higher or lower loadings.

### 3.8. XPS analysis

Comparative investigations were undertaken to determine the surface chemical states of Ce, Fe, Mn, and O species for  $\text{FeMnO}_x$ ,  $\text{FeMnO}_x\text{-S}$ , Ce(y) ( $y=5, 10$  and 12.5% ceria) and Ce(12.5)-S catalysts (Fig. 9). It can be observed in Fig. 9A that two major regions are observed in Ce spectra, 882–896 eV and 898–917 eV, coinciding with  $\text{Ce } 3d_{5/2}$  and  $\text{Ce } 3d_{3/2}$  respectively. These regions and the resulting signals are in agreement with values observed in works related to ceria based solid solutions [32]. Two common peak fitting models exist for deconvolution of the Ce signals, the first utilises an 8 peak fitting pattern, in this instance only 2 peaks are considered for their contribution to the total  $\text{Ce}^{3+}$ , however this can lead to underestimation of the real values, while arguably retaining the effective trend [57]. The more reliable model utilises 10 individual peak assignments;  $v_0, v, v', v''$  and  $v'''$ , which are associated with deconvoluted signals in the  $\text{Ce } 3d_{5/2}$  region and  $u_0, u, u', u''$  and  $u'''$  in the  $\text{Ce } 3d_{3/2}$  region, four of these ( $v_0/u_0$  and  $v'/u'$ ) are ascribed to  $\text{Ce}^{3+}$  and 6 ( $v/u, v''/u''$  and  $v'''/u'''$ ) to  $\text{Ce}^{4+}$  [32]. Fig. 9B illustrates the

spectra obtained for Fe, two distinguishable signals are observed  $\text{Fe } 2p_{3/2}$  (710.0–711.0 eV) and  $\text{Fe } 2p_{1/2}$  (723.5–724.5 eV). Peak fitting deconvolution of the  $\text{Fe } 3d_{3/2}$  peak indicates the presence of two different Fe species,  $\text{Fe}^{2+}$  (710.0–710.6 eV) and  $\text{Fe}^{3+}$  (712.4–712.7 eV). The same deconvolution procedure was applied for the  $\text{Mn } 3p_{3/2}$  signal in Fig. 9C, it can be reliably separated into three contributing signals 640.5–641.1 eV, 642.2–643.0 eV and 645.5–646.8 eV. The position of samples not treated with  $\text{SO}_2$  are similar to those observed for  $\text{Mn } 3p_{3/2}$  in  $\text{CrMnO}_x$  systems [20], hence these signals can be assigned to  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  respectively. It has been shown previously that treatment of catalysts with  $\text{SO}_2$  results in increased binding energy of transition metal ions [58], which may occur outside of the normally anticipated eV range.

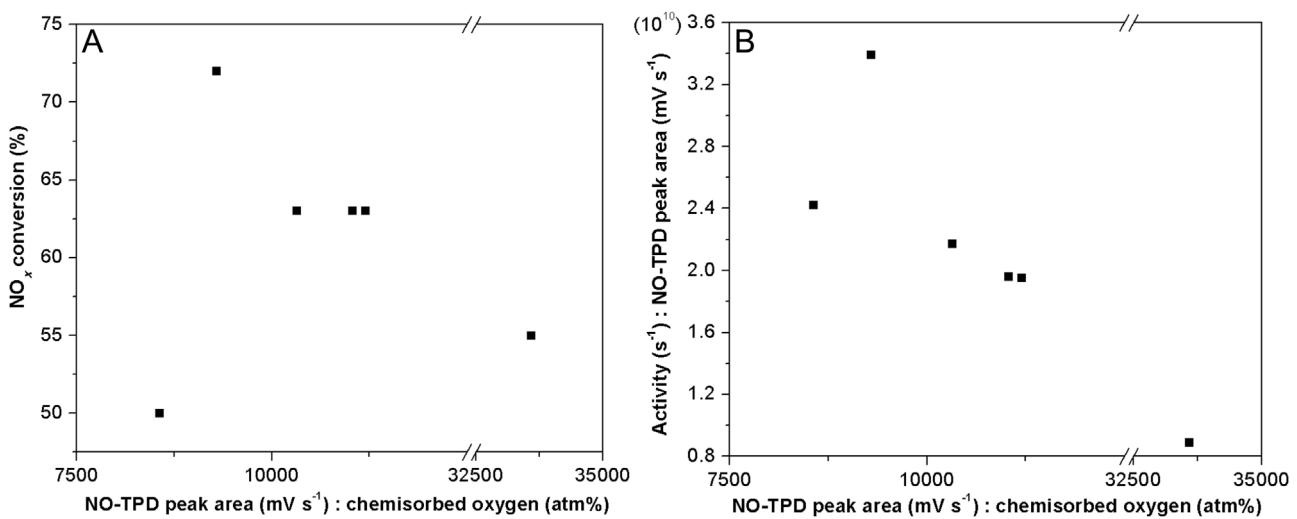
Table 3 displays the determined surface concentration (atm.%) of the catalysts.  $\text{FeMnO}_x$  exhibits a surface enrichment of Fe (0.33) as determined from  $\text{Fe}/(\text{Fe} + \text{Mn})$ , however the ceria modified samples have effectively the same ratio of 0.29–0.30, which is lower than the theoretical bulk composition (0.4). The highest surface concentration of metals was found for  $\text{FeMnO}_x$ , the addition of ceria in all instances resulted in a significant decline of the surface quantities of both Fe and Mn, however, of the modified variants Ce(12.5) exhibits maximised surface Fe and Mn concentrations. It can be observed in Fig. 9D and Fig. S1 that asymmetric peaks were observed in the O 1 s spectra of all samples, deconvolution of these signals leads to two distinctly different peaks, 529.3–529.9 eV, which is assigned to lattice oxygen ( $\text{O}^{2-}$ ) and 531.1–531.5 eV, which can be attributed to several forms of oxygen species such as, chemisorbed  $\text{O}_2^{2-}$  or  $\text{O}^-$  species [31,32].

Table 4 displays calculated concentrations of Fe, Mn and O species. It has been suggested previously that surface chemisorbed oxygen species play a significant role in oxidation reactions [5]. NO oxidation is suggested to play a crucial role in low-temperature SCR [20], hence it may be expected that the most active catalyst possess the largest amount of active oxygen species [42,59], however, this is not the case (Table 4). The most active catalyst, has less chemisorbed oxygen at its surface than a number of the other catalyst, but it also has the lowest O 1s binding energy, indicating improved oxygen mobility. NO oxidation is known to be the rate limiting step if the fast SCR reaction proceeds via the L-H mechanism, however for the E-R mechanism  $\text{NO}_2$  desorption dominates the reaction kinetics. On related mixed metal oxide catalysts NO oxidation has been suggested to proceed via the L-H mechanism, hence, chemisorbed surface oxygen and NO adsorption are key parameters for enhanced activity [20,42]. To try and elucidate the major factor affecting the activity of these catalysts the obtained conversions for  $\text{FeMnO}_x$  and Ce(y) (where  $y=5\text{--}15$  mol% ceria addition) were plotted against the ratio between their total NO desorption area ( $\text{mV s}^{-1}$ ) and surface O (atm.%) (Fig. 10A),

**Table 4**

Binding Energies (eV) and surface speciation of  $\text{FeMnO}_x$ ,  $\text{FeMnO}_x\text{-S}$ , Ce(y) ( $y=5, 10$  and 12.5%) and Ce(12.5)-S.

Catalyst	Surface concentration (atm.%)						
	$\text{Fe } 2p_{3/2}$ (eV)		$\text{Mn } 2p_{3/2}$ (eV)			$\text{O } 1s$ (eV)	
	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$	$\text{Mn}^{2+}$	$\text{Mn}^{3+}$	$\text{Mn}^{4+}$	$\text{O}^{2-} (\text{O}_\alpha)$	$\text{O}^-/\text{O}_2^{2-} (\text{O}_\beta)$
$\text{FeMnO}_x$	<b>710.0</b>	<b>712.0</b>	<b>640.6</b>	<b>642.1</b>	<b>644.8</b>	<b>529.6</b>	<b>531.5</b>
	4.40	6.43	8.55	8.02	5.70	48.70	18.20
$\text{FeMnO}_x\text{-S}$	<b>710.7</b>	<b>7133</b>	<b>640.5</b>	<b>642.6</b>	<b>645.0</b>	<b>530.1</b>	<b>531.9</b>
	3.80	4.12	9.76	6.75	583	39.12	30.62
Ce(5)	<b>710.2</b>	<b>712.4</b>	<b>641.2</b>	<b>642.6</b>	<b>644.9</b>	<b>529.6</b>	<b>531.5</b>
	3.08	4.43	6.98	6.33	4.78	45.15	28.87
Ce(10)	<b>710.3</b>	<b>7125</b>	<b>641.1</b>	<b>642.5</b>	<b>644.9</b>	<b>529.5</b>	<b>531.3</b>
	3.04	4.00	6.72	5.68	4.61	46.75	28.65
Ce(12.5)	<b>710.5</b>	<b>712.6</b>	<b>641.3</b>	<b>642.5</b>	<b>644.9</b>	<b>529.3</b>	<b>531.3</b>
	3.68	4.55	6.88	678	5.71	49.06	22.66
Ce(12.5)-S	<b>710.6</b>	<b>712.7</b>	<b>641.3</b>	<b>642.5</b>	<b>645.2</b>	<b>529.9</b>	<b>531.5</b>
	3.71	3.91	6.66	6.45	5.18	42.47	31.14



**Fig. 10.** NO<sub>x</sub> conversion (%) against NO-TPD peak area (mV s<sup>-1</sup>): chemisorbed oxygen (atm%) (A), Activity (s<sup>-1</sup>): NO-TPD peak area (mV s<sup>-1</sup>) against NO-TPD peak area (mV s<sup>-1</sup>): chemisorbed oxygen (atm%) (B). (NO-TPD peak area refers to values corrected against the mass of catalyst used in reaction (2.6 g) compared to TPD (100 mg), which are representative of total NO adsorption sites and chemisorbed surface oxygen O<sub>B</sub>, determined via XPS).

which is representative of the ratio between the NO adsorption sites and chemisorbed surface oxygen. Little can be ascertained from this data, except for the fact that there appears to be a trend similar to a volcano plot, however it is not possible to discern the differences between catalysts containing 5–10 mol% ceria. To further explore this trend, the conversions were converted to activity values (s<sup>-1</sup>) and corrected against the NO-TPD peak area, giving final values comparable to turnover numbers. Plotting these values against the NO adsorption sites to chemisorbed surface oxygen ratio (Fig. 10B) a more convincing volcano plot is established, which demonstrates that all catalysts containing ceria exhibit enhancements in turnover, which are between 2 and 4 times greater than FeMnO<sub>x</sub> at 75 °C. This indicates a clear effect on the catalytic activity which appears to be attributable to the fast-SCR reaction. The standard SCR reaction is known to be heavily reliant upon NH<sub>3</sub> adsorption sites, which when increased gives rise to higher conversion [60–62]. However in these systems a notable decrease is found in the number of NH<sub>3</sub> adsorption sites, in conjunction with an increase in conversion, suggesting that standard SCR plays a minor role compared to fast-SCR. Hence, ceria appears to tune the catalytic surface by adjusting the ratio between NO adsorption sites

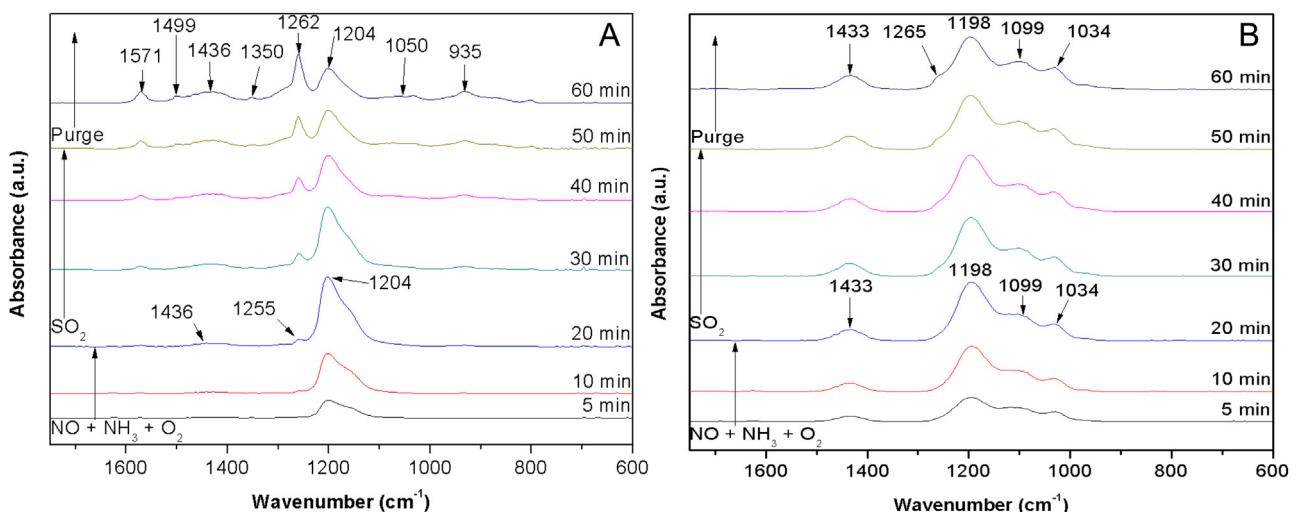
**Table 5**

Surface atomic concentration of Ce<sup>3+</sup> and Ce<sup>4+</sup> of Ce(y) (y=5, 10 and 12.5%) and Ce(12.5)-S.

Catalyst	Surface ratio		Surface concentration (atm.%)		
	Ce <sup>3+</sup> / (Ce <sup>3+</sup> + Ce <sup>4+</sup> )	Ce <sup>4+</sup> / (Ce <sup>3+</sup> + Ce <sup>4+</sup> )	Ce	Ce <sup>3+</sup>	Ce <sup>4+</sup>
Ce(5)	0.44	0.56	0.38	0.17	0.21
Ce(10)	0.36	0.64	0.56	0.20	0.36
Ce(12.5)	0.32	0.68	0.68	0.22	0.46
Ce(12.5)-S	0.47	0.53	0.48	0.23	0.25

and chemisorbed surface oxygen, which when optimised gives a significant enhancement in the activity of the catalyst.

Examination of the SO<sub>2</sub> treated catalysts shows that FeMnO<sub>x</sub> and Ce(12.5)-S exhibit significantly different surface compositions and increased binding energies of all observed species as a result of SO<sub>2</sub> exposure (Tables 4 and 5). It was found over FeMnO<sub>x</sub> that very little change occurred in the total surface Mn concentration, however it was noted that there was an apparent increase in the



**Fig. 11.** *In-situ* DRIFTS of FeMnO<sub>x</sub> and Ce(12.5), for the first 20 min the catalysts are exposed to a mixture of NO, NH<sub>3</sub>, O<sub>2</sub> and N<sub>2</sub> (0.1%, 0.1%, 3% and balance respectively) at a total flow rate of 150 mL min<sup>-1</sup>. After 20 min the gas is switched for 100 ppm SO<sub>2</sub> in N<sub>2</sub> at a total flow rate of 150 mL min<sup>-1</sup>.

Mn<sup>2+</sup> concentration and a decrease in Mn<sup>3+</sup>. A significant alteration was observed in the total Fe surface concentration, Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations decreased substantially during exposure to SO<sub>2</sub>. The surface lattice oxygen was found to decline significantly and a comparable increase in chemisorbed oxygen was observed, suggesting the interaction and conversion of SO<sub>2</sub> at the surface of the catalyst [19]. Ce(12.5) exhibits an entirely different change to its surface after exposure to SO<sub>2</sub>, it is found that all elements decline slightly (Tables 4 and 5), except for oxygen, which exhibits a trend similar to that found for FeMnO<sub>x</sub>. However the reduction in lattice oxygen and subsequent increase in active oxygen is not as severe as FeMnO<sub>x</sub>. The apparent attenuated modification of the surface as opposed to significant loss of one surface species, namely Fe<sup>2+</sup> may help to explain the higher NO<sub>x</sub> conversion exhibited by Ce(12.5) after SO<sub>2</sub> exposure.

### 3.9. In-situ DRIFTS SO<sub>2</sub> poisoning experiments

*In-situ* DRIFTS was conducted in the presence of SO<sub>2</sub> to further study the deactivation of FeMnO<sub>x</sub> in comparison to the resistance exhibited by Ce(12.5) (Fig. 11). To determine the initially adsorbed species associated with the reaction, a mixture of NO, NH<sub>3</sub>, O<sub>2</sub> and N<sub>2</sub> were flowed over the catalysts for 20 min (Figs. 11A and 11B). It can be observed that FeMnO<sub>x</sub> (Fig. 11A) over the initial 20 min introduction of gas exhibits two major features *ca.* 1463 and 1204 cm<sup>-1</sup>. On the basis of several literature sources these may be attributed to NH<sub>4</sub><sup>+</sup> bound to Brønsted acid site and the significantly stronger of the two peaks with the formation of coordinated NH<sub>3</sub> on Lewis acid sites [63], a small peak appearing at 1255 cm<sup>-1</sup> is also observed, which coincides with the formation of a bridged nitrate [63]. The system was then purged with nitrogen at 120 °C and 100 ppm SO<sub>2</sub> was fed over the catalyst for 30 min, during this time several new peaks are observed and grow in accordance with exposure to SO<sub>2</sub>, 935, 1050, 1262, 1350, 1436, 1499 and 1571 cm<sup>-1</sup>. It is found that these features grow in tandem with significant reduction of the signal at 1204 cm<sup>-1</sup> showing that SO<sub>2</sub> competitively adsorbs over the catalyst and occupies sites by forming sulphate species (1262, 1050 cm<sup>-1</sup> and 935 cm<sup>-1</sup>), SO<sub>3</sub> species (1436 cm<sup>-1</sup>) and surface sulphate species with a single S=O bond (1344 cm<sup>-1</sup>). HSO<sub>4</sub><sup>-</sup>(1571 cm<sup>-1</sup>) [64] are also present and found to increase with SO<sub>2</sub> exposure time verifying the formation of an important intermediate of NH<sub>4</sub>HSO<sub>4</sub>. On this basis it can be suggested that the formation of NH<sub>4</sub>SO<sub>4</sub> is, in part, responsible for the deactivation observed over FeMnO<sub>x</sub> [30,34]. It is demonstrated that all species remain stable over the catalyst after purging with nitrogen for 10 min, indicating the irreversible nature of the deactivating effect of sulphur species on this catalyst. Similar positions for NH<sub>4</sub><sup>+</sup> on Brønsted acid sites (1433 cm<sup>-1</sup>) and Lewis acid coordinated NH<sub>3</sub> (1198 cm<sup>-1</sup>) are observed over Ce(12.5) (Fig. 11B). Additional adsorbed species are also found, namely arising from *cis*-N<sub>2</sub>O<sub>2</sub><sup>2-</sup> (1034 cm<sup>-1</sup>) and *trans*-N<sub>2</sub>O<sub>2</sub><sup>2-</sup> (1099 cm<sup>-1</sup>) [65]. Introduction of SO<sub>2</sub> results in the appearance of a small shoulder (*ca.* 1265 cm<sup>-1</sup>) after 30 min, indicating significant reduction of sulphate formation compared to FeMnO<sub>x</sub>. Based upon these observations, it can be suggested that nitrogen containing species are much more stable over the Ce(12.5) catalyst compared to FeMnO<sub>x</sub>, indicating that competitive adsorption is significantly reduced over Ce(12.5) during the timescales of this study. Similarly no signals relating to HSO<sub>4</sub><sup>-</sup> (1571 cm<sup>-1</sup>), SO<sub>3</sub> species (1436 cm<sup>-1</sup>) or surface bound sulphate (1344 cm<sup>-1</sup>) were observed, demonstrating the enhanced stability of the catalyst in the presence of SO<sub>2</sub>. It can be determined, that the FeMnO<sub>x</sub> catalyst exhibits significant adsorption of SO<sub>2</sub> which leads to irreversible deactivation caused by sulphate/sulphite formation on the surface of the catalyst, in conjunction with the formation of HSO<sub>4</sub><sup>-</sup>, an intermediate of NH<sub>4</sub>HSO<sub>4</sub>, which leads to gradual pore

blockage. Conversely Ce(12.5) results in very minor formation of bulk sulphate after 30 min of exposure to SO<sub>2</sub>, demonstrating an improved resistance of the catalyst towards SO<sub>2</sub>.

## 4. Conclusions

The influence of ceria addition to FeMnO<sub>x</sub> upon low-temperature SCR catalytic activity and SO<sub>2</sub> resistance was examined. Catalysts containing CeO<sub>x</sub> exhibited increased concentration of chemisorbed surface oxygen compared to FeMnO<sub>x</sub>, in conjunction with lower NO and NH<sub>3</sub> adsorption, which resulted in improved turnover 2–4 times greater than FeMnO<sub>x</sub>. This enhancement effect is attributed to the fast–SCR reaction, which is favoured by reduced NH<sub>3</sub> adsorption and a suitable ratio between NO sites and chemisorbed surface oxygen. Both catalysts were found to be affected via the introduction of SO<sub>2</sub> during SCR. However Ce(12.5) possessed significant recovery after stopping SO<sub>2</sub>, no loss of pore volume was found, though a small loss of surface area and a general reduction of surface species occurred. Ce(12.5) possessed stable N-containing surface species, which resulted in very little metal sulphate and no obvious NH<sub>4</sub>HSO<sub>4</sub> formation, leading to enhanced sulphur resistance.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.01.019>.

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